
फेरोक्रोमियम का रासायनिक विश्लेषण

(पहला पुनरीक्षण)

Methods of Chemical Analysis of Ferrochromium

(*First Revision*)

ICS 77.100

© BIS 2019



भारतीय मानक ब्यूरो

BUREAU OF INDIAN STANDARDS

मानक भवन, 9 बहादुरशाह ज़फ़र मार्ग, नई दिल्ली-110002

MANAK BHAVAN, 9 BAHADUR SHAH ZAFAR MARG
NEW DELHI-110002

www.bis.org.in www.standardsbis.in

FOREWORD

This Indian Standard was adopted by the Bureau of Indian Standards, after the draft finalized by the Chemical Analysis of Metals Sectional Committee had been approved by the Metallurgical Engineering Division Council.

The earlier Indian Standard on methods of chemical analysis of ferrochromium were covered by the following parts:

<i>IS No.</i>	<i>Title</i>
13452	Methods of chemical analysis of ferrochromium
(Part 1):1992	Determination of silicon in high carbon ferrochromium by gravimetric method
(Part 2): 1992	Determination of silicon in low carbon ferrochromium by gravimetric method
(Part 3): 1992	Determination of phosphorus in low carbon ferrochromium by spectrometric method
(Part 4): 1992	Determination of total sulphur in low carbon and high carbon ferrochromium by direct combustion method.
(Part 5): 1992	Determination of chromium in high carbon ferrochromium/charge chrome by dichromate titration (<i>first revision</i>)
(Part 6): 1997	Determination of chromium in low carbon ferro chromium
(Part 7):2003	Determination of phosphorus in Ferrochromium/charge chrome by alkalimetric

The Committee while revising this standard decided to have a single standard by merging all the above seven parts of IS 13452. With the publication of this standard all the above seven parts of IS 13452 will be superseded.

In this revision instrumental methods of determination of manganese, phosphorus and titanium by spectrophotometric method and chromium by X-ray fluorescence method have been incorporated.

Assistance has been derived from ISO 4140 'Ferrochromium and ferrosilicochromium — Determination of chromium content potentiometric method' issued by International organization of standardization.

For the purpose of deciding whether a particular requirement of this standard is complied with, the final value, observed or calculated, expressing the result of a test or analysis, shall be rounded off in accordance with IS 2 : 1960 'Rules for rounding off numerical values (*revised*)'. The number of significant places retained in the rounded off value should be the same as that of the specified value in this standard.

Indian Standard

METHOD OF CHEMICAL ANALYSIS OF FERROCHROMIUM

(*First Revision*)

1 SCOPE

This standard describes the chemical analysis of ferrochromium.

2 REFERENCES

The standards given below contain provisions which through reference in this text, constitute provisions of this standard. At the time of publication, the editions indicated were valid. All standards are subject to revision and parties to agreements based on this standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below:

<i>IS No.</i>	<i>Title</i>
264 : 2005	Nitric acid (<i>third revision</i>)
265 : 1993	Hydrochloric acid (<i>fourth revision</i>)
266 : 1993	Sulphuric acid (<i>third revision</i>)
1070 : 1992	Reagent grade water (<i>third revision</i>)
1472 : 1977	Methods of sampling of ferroalloys for determination of chemical composition (<i>first revision</i>)

3 SAMPLING

The sample shall be drawn and prepared in accordance with IS 1472.

4 QUALITY OF REAGENTS

Unless specified otherwise, analytical grade reagents and distilled water (*see* IS 1070) shall be employed for the test.

5 DETERMINATION OF SILICON IN HIGH CARBON FERROCHROMIUM BY GRAVIMETRIC METHOD (CONTAINING CARBON ABOVE ONE PERCENT)

5.1 Outline of the Method

The sample is decomposed by fusion with sodium peroxide and silicic acid dehydrated from the acidified extract by fuming with perchloric acid and finally estimated gravimetrically.

5.2 Reagents

5.2.1 Sodium Peroxide — solid (yellow granular).

5.2.2 Sodium Carbonate — solid.

5.2.3 Hydrochloric Acid — rd = 1.16 (*see* IS 265).

5.2.4 Perchloric Acid — 60 percent.

5.2.5 Hydrofluoric Acid — 40 percent.

5.2.6 Dilute Hydrochloric Acid — 2 percent (v/v).

5.2.7 Dilute Sulphuric Acid — 50 percent (v/v).

5.2.8 Silver Nitrate Solution — 2 percent (m/v).

5.3 Procedure

5.3.1 Weigh 0.500 g of finely ground dried sample into a nickel crucible containing 5 g of sodium peroxide and 2 g of anhydrous sodium carbonate. Mix well and cover with 2 g of sodium peroxide. Fuse the content carefully over the dull flame of Mecker burner or in a muffle furnace at a temperature 550 to 600 °C. Care should be taken not to raise the temperature rapidly as to cause spattering. When the mass is molten, a slight rotary motion is imparted to the crucible to stir up any unattached particles of alloy on the bottom or sides. The temperature is to be increased to a bright redness for a minute just before completion of fusion. If followed carefully, a very quiet fusion without any spattering will result. After the crucible has cooled, slowly drop the crucible with its solidified melt in 50 ml of cold water in a 500 ml Polytetra fluoroethylene (PTFE) beaker and cover with PTFE cover glass. When the reaction has subsided take out crucible and wash with warm hydrochloric acid (10 percent) and then with water collecting all the washings in the same PTFE beaker.

5.3.2 Acidify the extract (*see* 5.3.1) by adding 50 ml of hydrochloric acid and then transfer the solution to a 500 ml glass beaker, evaporate to almost syrupy stage and add 30 ml of perchloric acid and keep the beaker on hot plate until white perchloric acid fumes are refluxed for 15 min.

NOTE — The dehydration of the silica in high carbon ferrochromium can be carried out even by sulphuric acid, but the difficulties are frequently encountered due to the insolubility of basic chromic salts due to the presence of high chromium

content of the alloy. By fuming with perchloric acid for dehydration, this sort of difficulty will not occur as perchlorates are easily soluble even in cold water.

5.3.3 Cool solution (*see* 5.3.2) and add 20 ml of hydrochloric acid (50 percent) and dilute with distilled water. Boil, cool and filter the silica on an ashless medium textured filter paper placed on the fluted glass funnel. Rinse the beaker with warm water using bobby and transfer the content to the filter paper. Wash with warm hydrochloric acid. Then finally wash several times with hot water till it is free from chloride.

NOTE — Check the solution for precipitation of chloride by silver nitrate solution (2 percent).

5.3.4 Transfer the residue on (*see* 5.3.3) along with the filter paper to a platinum crucible. Evaporate to dryness and ignite at temperature of 1 100 °C to a constant mass. Allow to cool in a desiccator and weigh the crucible containing impure silica (*A*).

5.3.5 Moisten the impure silica with few drops of water and add about 2 or 3 drops of dilute sulphuric acid (50 percent). Add about 5 ml of hydrofluoric acid and evaporate to dryness until fumes cease to evolve. Ignite in a muffle furnace at 1 100 °C to a constant mass. Allow to cool in a desiccator and weigh the crucible (*B*).

5.3.6 Blank

Carry out a blank determination following the procedure specified in 5.3.1 to 5.3.5 and using same amount of all reagents. Correct the final results for the blank value, if any (*C*).

5.4 Calculation

$$\text{Silicon, percent by mass} = \frac{[(A - B) - C] \times 46.74}{D}$$

where

A = mass of crucible before hydrofluorization, in g;

B = mass of crucible after hydrofluorization, in g;

C = mass of silica from the blank, in g; and

D = mass of sample taken, in g.

6 DETERMINATION OF SILICON BY GRAVIMETRIC METHOD IN LOW CARBON FERROCHROMIUM (CONTAINING CARBON UP TO ONE PERCENT)

6.1 Outline of the Method

After dissolution of the sample, silicic acid is dehydrated by fuming with perchloric acid. The solution is filtered and the silica is ignited, weighed and then volatilized with hydrofluoric acid. The residue is ignited

and weighed; the loss in weight represents silica.

6.2 Reagents

6.2.1 Hydrochloric Acid — rd = 1.16 (*see* IS 265).

6.2.2 Perchloric Acid — 60 percent.

6.2.3 Hydrofluoric Acid — 40 percent.

6.2.4 Dilute Sulphuric Acid — 50 percent.

6.2.5 Silver Nitrate Solution — 2 percent (*m/v*).

6.3 Procedure

6.3.1 Weigh accurately 1.00 g of sample into a 400 ml glass beaker, add 20 ml of hydrochloric acid and heat until effervescence ceases and sample dissolves completely.

6.3.2 When the beaker has cooled down add 20 to 25 ml of perchloric acid (60 percent) and heat to fuming and reflux for 15 min and cool. Add 2 to 3 ml of hydrochloric acid and dilute with distilled water. Boil and filter the silica through ashless, medium textured filter paper. Rinse the beaker with warm water and transfer the contents to the filter.

6.3.3 Wash the residue with warm hydrochloric acid and then finally wash several times with hot water, till it is free from chloride.

NOTE — Check the filtrate for presence of chloride using silver nitrate solution (2 percent).

6.3.4 Transfer the residue on (*see* 6.3.3) along with the filter to a platinum crucible. Evaporate to dryness and ignite at 1 100 °C in a muffle furnace to a constant mass. Cool in a desiccator and weigh the crucible (*A*).

6.3.5 Moisten the impure silica (*see* 6.3.4) with a few drops of water. Add about 10 ml of hydrofluoric acid and 2 or 3 drops of dilute sulphuric acid (50 percent) and cautiously evaporate to dryness. Ignite at 1 100 °C to a constant mass. Allow to cool in a desiccator and weigh the crucible (*B*).

6.3.6 Blank

Carry out a blank determination following the procedure specified in 6.3.2 to 6.3.5 and using same amount of all reagents. Correct the final results for the blank value, if any (*C*).

6.4 Calculation

$$\text{Silicon, percent by mass} = \frac{[(A - B) - C] \times 46.74}{D}$$

where

A = mass of crucible before hydrofluorization, in g;

B = mass of crucible after hydrofluorization, in g;

C = mass of silica from the blank, in g; and

D = mass of sample taken, in g.

7 DETERMINATION OF PHOSPHORUS BY SPECTROPHOTOMETRIC METHOD IN LOW CARBON FERROCHROMIUM (CONTAINING CARBON UP TO ONE PERCENT)

7.1 Outline of the Method

Sample is dissolved in hydrochloric acid, nitric acid and perchloric acid, when phosphorus is oxidized to orthophosphoric acid. Fume with perchloric acid, after addition of sodium chloride to remove chromium as chromyl chloride. The phosphorous in the solution is reacted with ammonium molybdate and reduced with hydrazine sulphate solution to give molybdenum blue. The intensity of the colour is measured spectrophotometrically at 820 nm.

7.2 Reagents

7.2.1 Hydrochloric Acid — rd = 1.16 (see IS 265).

7.2.2 Dilute Hydrochloric Acid — 35 percent (v/v).

7.2.3 Nitric Acid — rd = 1.42 (see IS 264).

7.2.4 Perchloric Acid — 60 percent.

7.2.5 Dilute Sulphuric Acid — 1 : 4, 3 : 5 (v/v).

7.2.6 Aqua Ammonium

7.2.7 Sodium Chloride — Solid.

7.2.8 Sodium Sulphite (Na_2SO_3) Solution — 10 percent (m/v) should be freshly prepared.

7.2.9 Ammonium Molybdate Solution — Solution (A). Add 20 g of ammonium molybdate $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot\text{H}_2\text{O}]$ to 100 ml of warm water. Add 800 ml of dilute sulphuric acid (3 : 5) and cool to room temperature. Make up the volume to 1 litre with water.

7.2.10 Hydrazine Sulphate Solution — Solution (B). Dissolve 1.5 g of hydrazine sulphate ($\text{N}_2\text{H}_4\cdot\text{H}_2\text{SO}_4$) in 1 litre water.

7.2.11 Phosphorus Standard Solution — (1 ml = 0.1 mg P). Weigh accurately 2.292 g of anhydrous sodium hydrogen phosphate (Na_2HPO_4) previously dried at 105°C. Transfer to 500 ml volumetric flask. Dissolve in 100 ml of water, dilute to mark and mix. Pipette out 10 ml of solution and dilute to 100 ml with water.

7.2.12 Colour Development Solution — Mix 25 ml of solution (A) and 10 ml of solution (B) and make up the volume to 100 ml with water. This should be prepared just before use.

7.3 Procedure

7.3.1 Weigh accurately 0.500 g of sample and transfer

to 250 ml beaker. Wet the sample with 10 ml of water. Add 20 ml hydrochloric acid, 5 ml nitric acid and 25 ml perchloric acid and reflux for 15 min after fuming starts. Keep it on the hot plate for dissolution for about 30 min till the mass in the beaker becomes clear.

7.3.2 Add dilute hydrochloric acid (35 percent) dropwise, till the solution turns green. Keep on a hot plate and reflux for 5 min.

7.3.3 Repeat the operation (see 7.3.2), 3 or 4 times and finally add a pinch of sodium chloride and reflux till all the chromium is expelled and no more brown fumes are observed.

7.3.4 Cool solution (see 7.3.3) and add about 40 ml of water to dissolve the soluble salts and make up the volume to 100 ml into a volumetric flask. Filter the solution using medium textured filter paper and collect the filtrate in a 250 ml beaker.

7.3.5 Pipette out 10 ml of filtrate (see 7.3.4) in to a 250 ml beaker. Add 10 ml of sodium sulphite solution (freshly prepared) and 10 ml of water. Boil for 1 min.

7.3.6 Add 25 ml of colour development solution (see 7.2.12) and immerse the beaker in a boiling water bath and keep it for 10 min for full colour development. Cool to room temperature and make up the volume to 100 ml with distilled water in volumetric flask.

7.3.7 Transfer a suitable portion of 7.3.6 to 1 cm cell and adjust the spectrophotometer at 820 nm and measure the absorbance against the reagent blank.

7.3.8 Blank

Carry out a blank determination using same amount of reagents and chemicals and following the procedure specified in 7.3.1 to 7.3.7.

7.3.9 Preparation of the Calibration Curve

Transfer 0, 1, 2, 3, 4 and 5 ml of standard phosphorus solution (1 ml = 0.1 mg P) (see 7.2.11) to 500 ml beaker and proceed according to 7.3.1 to 7.3.7. The flask containing the zero ml of phosphorus solution is regarded as blank and the net value of spectrophotometric reading is plotted against mg of phosphorus.

7.3.10 Convert the spectrophotometric readings of test solution to mg of phosphorus obtained from calibration curve and calculate the percentage of phosphorus.

7.4 Calculation

$$\text{Phosphorus, percent by mass} = \frac{A}{B} \times \frac{1}{10}$$

where

A = mass, of phosphorus found in solution; in mg; and

B = mass, of the sample taken; in g.

8 DETERMINATION OF TOTAL SULPHUR IN THE RANGE FROM 0.005 TO 0.5 PERCENT IN LOW CARBON AND HIGH CARBON FERROCHROMIUM BY DIRECT COMBUSTION METHOD

8.1 Outline of the Method

The sulphur in the sample is converted to sulphur dioxide by combustion in stream of oxygen in a furnace at 1 600 °C. It is then absorbed in hydrochloric acid solution and titrated with standard potassium iodate solution, using starch as indicator.

8.2 Reagents

8.2.1 Dilute Hydrochloric Acid — 3 percent (v/v).

8.2.2 Accelerators — For example, iron, tin, etc, free from sulphur.

8.2.3 Potassium Iodate Standard Solution — (1 ml = 0.1 mg S)— Dissolve 0.222 5 g of potassium iodate in 900 ml of water and dilute to 1 litre.

8.2.3.1 Potassium iodate standard solution (1ml = 0.1mg S.—Transfer 10 ml of potassium iodate standard solution (see 8.2.3) to a 100 ml volumetric flask, make up with water and mix well.

8.2.4 Starch Solution — Transfer 1.00 g of pure starch powder and 2 ml of water in a small beaker and stir until a smooth paste is obtained. Pour this mixture into 50 ml of boiling water. Cool, add 1.5 g potassium iodate

and stir until dissolved. Dilute to 100 ml. This solution is to be prepared afresh every time.

8.2.5 Standard Sample — It should be of known sulphur content in the range of interest.

8.2.6 Ceramic Boats/Crucibles — Pre-ignited at 1100°C and kept in a dessicator.

8.3 Apparatus

The apparatus consists of three parts namely,

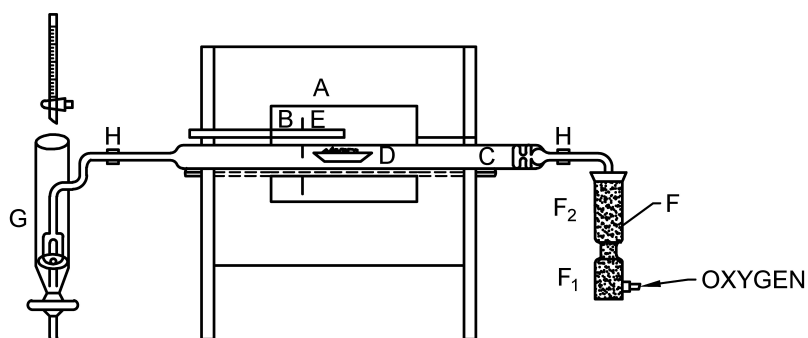
- oxygen-cylinder and purifier *F* (containing soda asbestos, F_1 and magnesium perchlorate, F_2);
- a furnace capable of reaching a temperature 1600°C with combustion tube and ceramic filter; and
- the absorption and titration assembly.

The three parts are connected with one other by tubes and hermetically sealed with stoppers as shown in Fig. 1.

8.4 Procedure

8.4.1 Arrange the apparatus as given in 8.3.1.

8.4.2 Switch on the furnace with oxygen bubbling through absorption vessel, previously filled with dilute hydrochloric acid (3 percent). Add 2 ml of starch solution to the vessel. Adjust the flow of oxygen from 1.0 to 1.5 litre/min. Fill the burette with potassium



- A* = Combustion furnace
B = Temperature control
C = Combustion tube
D = Combustion boat
F = Oxygen purifiers (containing soda asbestos F_1 and anhydrous magnesium perchlorate F_2)
G = Absorption and titration apparatus
H = Rubber stopper and connecting tubes

FIG. 1 TITRATION ASSEMBLY FOR THE DETERMINATION OF SULPHUR

iodate solution and add to it the absorption solution dropwise till a blue colour is obtained.

8.4.3 Weigh 1 g of the standard sample and transfer it into a preignited boat/crucible. Add sufficient amount of accelerators (1 g of iron chips and 1 g of tin granules). After the unit has attained required warming, that is, about 30 min, introduce the boat/crucible with standard sample and accelerators in the furnace. Close the furnace. Burn the sample while passing oxygen all the time. Titrate continuously with potassium iodate solution at such a rate so as to maintain as close as possible to the original intensity of the blue colour.

NOTES

1 For low sulphur content, the standard potassium solution given in **8.2.3.1** may be used.

2 The end point may be detected if the blue colour is stable for 1 min without further addition of potassium iodate solution. Record the volume, in ml, of potassium iodate used (V_1).

8.4.4 Refill the titration vessel with dilute hydrochloric acid (3 percent). Add 2 ml of starch solution and follow the procedure specified in **8.4.3** using test sample. Titrate the absorption solution with potassium iodate to the preselected end point and record the volume, in ml, of potassium iodate used (V_3).

8.5 Blank

Determine the blank by placing the same amount of accelerator used in test sample in preignited crucible and following the same procedure as specified in **8.4.3**. Deduct the blank value (V_2) if any, from the final calculation.

8.6 Calculations

$$\text{Sulphur, percent by mass} = \frac{(V_3 - V_2) \times (M \times S)}{m \times (V_1 - V_2)}$$

where

- M = mass of standard sample, in g;
 S = percent of sulphur, in the standard sample;
 V_1 = volume of potassium iodate solution required for the titration of standard sample, in ml;
 V_2 = volume of potassium iodate solution required for the titration of blank, in ml;
 V_3 = volume of potassium iodate solution required for the titration of sample, in ml; and
 m = mass of test sample, in g.

9 DETERMINATION OF CHROMIUM IN THE RANGE OF 50 TO 70 PERCENT IN HIGH CARBON FERROCHROMIUM/CHARGE CHROME (CONTAINING CARBON ABOVE 1 PERCENT) BY DICHROMATE TITRATION

9.1 Outline of the Method

The sample is fused with sodium peroxide, leached in

water and acidified with sulphuric acid. Chromium is oxidized to dichromate by ammonium persulphate in the presence of silver nitrate. The chromium in solution is determined by adding excess of ferrous ammonium sulphate solution and back titrated to a purple end point with standard dichromate solution using sodium diphenylamine sulphonate as indicator to a purple end point.

9.2 Reagents

9.2.1 Sodium Peroxide — Solid.

9.2.2 Dilute Sulphuric Acid — 5 percent (v/v), 20 percent (v/v).

9.2.3 Ammonium Persulphate, solid.

9.2.4 Silver Nitrate Solution — 1 percent (w/v).

9.2.5 Phosphoric Acid — rd = 1.75 or 88 percent.

9.2.6 Potassium Permanganate Solution — 25 g/l.

9.2.7 Sodium Carbonate Anhydrous — solid.

9.2.8 Ferrous Ammonium Sulphate Solution — 0.1 N.

9.2.8.1 Dissolve 39.2 g of pure ferrous ammonium sulphate ($\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$) in 500 ml of dilute sulphuric acid (5 percent) in a 1 litre volumetric flask and make up to the mark with dilute sulphuric acid (5 : 95).

9.2.9 Standard Potassium Dichromate Solution — 0.1 N.

9.2.9.1 Dry potassium dichromate in an oven at 105 to 110 °C for one and a half hour, cool in a desiccator. Weigh exactly 4.903 5 g. Dissolve in water and transfer to 1 litre volumetric flask, dilute volume and mix.

9.2.10 Sodium Diphenylamine Sulphonate Indicator Solution — 0.2 percent (m/v).

9.2.10.1 Dissolve 0.2 g of sodium diphenylamine sulphonate in 100 ml hot distilled water.

9.2.11 Sodium Chloride Solution — 10 percent (w/v).

9.2.12 Concentrated Sulphuric Acid — rd = 1.84 (see IS 266).

9.2.13 Phosphoric and Sulphuric Acid Mixture — Take 1 200 ml of distilled water in a 2 litre capacity flat bottomed flask and to it add 400 ml of concentrated phosphoric acid followed by 400 ml of concentrated sulphuric acid and cool it under tap.

9.3 Procedure

9.3.1 Weigh 0.5 g of finely ground dried sample in a nickel crucible and add 8 g of sodium peroxide followed by 4 g of sodium carbonate and mix intimately. Add an additional 1 g of sodium peroxide. Cover the crucible

with lid and heat carefully over low temperature and finally fuse the mass over a flame/muffle furnace till completely fused.

9.3.2 Cool the melt. Place the crucible in a 500 ml beaker and dissolve. Remove the crucible and wash with water any particles adhering to the crucible. Add dilute sulphuric acid until it is acidic. Add further 30 ml and boil for 5 to 10 min. Cool and transfer to a 250 ml volumetric flask and dilute upto the mark with distilled water. Take an aliquot of 50 ml solution equivalent to 0.1 g of sample into a 1 litre conical flask.

9.3.3 Add 4 to 5 drops of potassium permanganate (KMnO_4) solution (25 g/l), if manganese is not present. Then add 10 ml of silver nitrate solution, warm to about 70 to 80°C and add about 4 to 5 g of ammonium persulphate. Keep on warm condition about 5 min and boil the solution for 10 min. If permanganate colour does not develop then add further 4 to 5 g of ammonium persulphate and boil. Continue boiling for about 30 min to destroy excess ammonium persulphate. Add 20 ml of sodium chloride solution (10 percent w/v) and again boil for 5 to 10 min till oxides of manganese or any permanganate disappears.

9.3.4 Cool the solution (*see 9.3.3*) to room temperature. Dilute to 350 ml. Add known quantity of ferrous ammonium sulphate till the colour is green and add an excess of 5 ml. Add 10 ml acid mixture (*see 9.2.13*) followed by 5 to 10 drops of sodium diphenylamine sulphonate indicator and dilute to about 400 ml with distilled water.

9.3.5 Titrate (*see 9.3.4*) the excess ferrous ammonium sulphate with standard potassium dichromate solution to a purple end point.

9.4 Blank

Run a blank determination following the procedure and using the same amount of all the reagents and titrate with standard dichromate solution using sodium diphenylamine sulphonate as indicator to a purple end point.

9.5 Calculation

$$\text{Chromium, percent by mass} = \frac{(V_1 - V_2)N \times 0.01734 \times 100}{M}$$

where

V_1 = volume of potassium dichromate solution required for ferrous ammonium sulphate used, in ml;

V_2 = volume, of potassium dichromate solution required for the back titration, in ml;

N = normality of potassium dichromate; and

M = mass of the sample taken, in g.

NOTE — If vanadium content in the material is more than 0.3 percent, use potassium permanganate, solution in place of potassium dichromate solution.

10 DETERMINATION OF CHROMIUM IN THE RANGE OF 60 TO 70 PERCENT IN LOW CARBON FERROCHROMIUM (CONTAINING CARBON UP TO 0.1 PERCENT AND SILICON LESS THAN 4 PERCENT) BY PERSULPHATE OXIDATION METHOD

10.1 Outline of the Method

After dissolution of the sample in a dilute sulphuric acid and phosphoric acid mixture and further treatment with nitric acid, chromium, manganese and vanadium (if present) are oxidized by ammonium persulphate in presence of silver nitrate catalyst. Permanganic acid is then destroyed by dilute hydrochloric acid. Chromium is reduced by ferrous ammonium sulphate and excess of ferrous ammonium sulphate is back titrated with standard potassium permanganate solution.

10.2 Reagents

10.2.1 Phosphoric Acid — Sulphuric Acid Mixture — To 600 ml of water, add cautiously 200 ml of sulphuric acid (rd = 1.84) and 100 ml of phosphoric acid (rd = 1.75). Mix, cool and dilute to 1 litre.

10.2.2 Concentrated Nitric Acid — rd = 1.42 (*see IS 264*).

10.2.3 Silver Nitrate Solution — 1 percent (w/v) — Dissolve 10 g of silver nitrate crystals in water and dilute to 1 litre.

10.2.4 Ammonium Persulphate Solution — Solid.

10.2.5 Dilute Hydrochloric Acid — 25 percent (v/v).

10.2.6 Dilute Sulphuric Acid — 5 percent (v/v).

10.2.7 Standard Potassium Permanganate Solution — 0.1 N.

10.2.7.1 Dissolve 3.2 g of potassium permanganate in 1 litre of water. Let it stand in the dark for 2 weeks. Filter without washing, through a gooch crucible or a fine porosity fitted glass crucible. Avoid contact with rubber or other organic material. Store in a dark coloured glass stoppered bottle.

10.2.7.2 Dry a portion of sodium oxalate at $105 \pm 5^\circ\text{C}$. Transfer 0.300 g of sodium oxalate to a 600 ml beaker. Add 200 ml of dilute sulphuric (5 percent) (previously boiled for 10 to 15 min and cooled) and heat to dissolve the oxalate. Titrate the hot oxalate solution at about 60 to 70°C with permanganate solution until a faint permanent pink colour persists for 30 s. Towards the end of titration one should take care to allow each drop to become decolourised before adding the next drop. To determine the blank, titrate 200 ml of dilute

hydrochloric acid (25 percent) treat as above with potassium permanganate solution to a faint pink colour. The blank correction is usually equivalent to 0.03/0.05 ml. Calculate the normality of potassium permanganate solution.

10.2.8 Ferrous Ammonium Sulphate Solution — 0.1 N approximate. Dissolve 39.2 g of ferrous ammonium sulphate in 1 litre of sulphuric acid (5 percent).

10.2.9 Phosphoric Acid — 20 percent (v/v).

10.3 Procedure

10.3.1 Weigh accurately about 0.500 g of the sample into a 400 ml beaker and add 25 to 30 ml of phosphoric acid and sulphuric acid mixture and keep it for dissolution on a hot plate. Heat until effervescence nearly ceases. Add cautiously 3 to 5 ml of concentrated nitric acid and evaporate to fumes. Cool the solution, dilute to about 100 ml and warm to dissolve salts. Transfer the solution to a 250 ml volumetric flask and make up the volume with water.

NOTE — Chromium forms sparingly soluble salts in the presence of nitric acid and concentrated sulphuric acid. It is, therefore, necessary to avoid excessive fuming.

10.3.2 Take 50 ml of aliquot (*see 10.3.1*) containing 0.1 g of sample and dilute to about 200 ml. Keep the solution for boiling on a hot plate, keeping glass rod in the beaker to prevent bumping at a later stage. While boiling add 20 ml of silver nitrate solution and add 4 to 5 drops of potassium permanganate (25 g/l) and then add 25 ml of freshly prepared ammonium persulphates solution (20 percent). Boil the solution for about 15 to 20 min. If a permanganate colour due to the presence of manganese in the sample does not develop within a few minutes add more silver-nitrate and ammonium persulphate solution and boil again for 10 to 15 min to decompose the excess of persulphate. To the boiling solution add 10 ml of dilute hydrochloric acid (25 percent) in small portions of 2 ml and continue boiling till permanganate colour disappears. In case either permanganate colour or any precipitated manganese dioxide do not disappear, add a little more of dilute hydrochloric acid (25 percent) and boil as before.

NOTE — During the process of boiling care should be taken to avoid losses of water by evaporation by adding water from time to time and thus always maintaining the original volume of the solution.

10.3.3 Cool the solution (*see 10.3.2*). Add a known excess of ferrous ammonium sulphate solution (0.1 N approximate) and 10 ml of phosphoric acid (20 percent). Stir and titrate the excess of ferrous ammonium sulphate solution with standard potassium permanganate solution (0.1 N) until a faint pink colour is obtained (V_2).

10.3.4 Blank

Boil the solution, till the permanganate colour is destroyed. Cool and add the same volume of ferrous ammonium sulphate as used for the sample. Titrate with standard potassium permanganate solution (0.1 N) to the appearance of pink colour (V_1).

10.4 Calculation

Calculate the chromium content as follow:

$$\text{Chromium, percent by mass} = \frac{(V_1 - V_2) \times N \times 0.01734 \times 100}{M}$$

where

V_1 = volume of standard permanganate required by the blank, in ml;

V_2 = volume of standard permanganate required in the experiment, in ml;

N = normality of the standard permanganate solution; and

M = mass of the sample in the aliquot taken, in g.

11 DETERMINATION OF CHROMIUM IN RANGE OF 60 TO 70 PERCENT IN LOW CARBON FERROCHROMIUM (CONTAINING CARBON UP TO 0.1 PERCENT AND SILICON MORE THAN 4 PERCENT) BY FUSION METHOD

11.1 Outline of the Method

After fusion of the sample with sodium peroxide and sodium carbonate instead of sulphuric acid and phosphoric acid same method is followed as given in 10.1.

11.2 Reagents

All the reagents given in 10.2.3 to 10.2.9 are used along with the following.

11.2.1 Sodium Peroxide — Solid.

11.2.2 Sodium Carbonate — Anhydrous.

11.3 Procedure

11.3.1 Transfer 0.5 g of the sample to a nickel crucible and add 8 g of sodium peroxide and 4 g of sodium carbonate and mix intimately. Cover the crucible and warm gently for about 5 min. Fuse the mixture over a low flame while imparting a swirling motion to the crucible. After holding molten mass for 3 min, increase the temperature to bright red for 1 min and allow it to cool.

11.3.2 Transfer the crucible and the fused mass to a 100 ml beaker, add hot water until the crucible is just submerged and heat gently until the melt is extracted. Remove the crucible and lid, washing with hot water

and boil the solution slightly. Cautiously acidify with dilute sulphuric acid (25 percent) and add 50 ml in excess. Add 20 ml of phosphoric acid (20 percent), cool and make up volume to 250 ml with distilled water in volumetric flask.

11.3.3 Take 50 ml of aliquot (*see 11.3.2*) containing 0.1 g of sample, in a 400 ml beaker and complete the determination following the same procedure as specified in steps **10.3.2** to **10.3.4** and calculate the percentage of chromium as given in **10.4**.

12 DETERMINATION OF CHROMIUM CONTENT IN FERROCHROMIUM BY POTENTIOMETRIC METHOD

12.1 Outline of the Method

Fusion of test portion with sodium peroxide, dissolution of the melt in water, and acidification of the aqueous solution with sulphuric acid. For some ferro alloys dissolution of a test portion by direct acid attack. Oxidation of chromium with ammonium persulphate in the presence of silver ions as catalyst. Determination of the sum of chromium and vanadium by potentiometric titration with ammonium iron(II) sulphate, and determination of the chromium content by difference.

12.2 Reagents

Unless specified otherwise, analytical grade reagents and distilled water (*see IS 1070*) shall be employed for the test.

12.2.1 Sodium peroxide — Solid.

12.2.2 Sodium Carbonate — Solid.

12.2.3 Ammonium Persulphate — Solid.

12.2.4 Urea

12.2.5 Phosphoric Acid — rd = 1.7 g/ml.

12.2.6 Nitric acid — rd = 1.42 (*see IS 264: 1976*).

12.2.7 Hydrofluoric Acid — 40 percent (v/v) solution.

12.2.8 Sulphuric Acid — 50 percent (v/v) solution.

To 400 ml water add cautiously 500 ml sulphuric acid (rd = 1.84 g/ml), mix, cool, dilute to 1 000 ml and mix.

12.2.9 Hydrochloric Acid — 40 percent (v/v) solution. To 600 ml water, add 400 ml hydrochloric acid (rd = 1.16 g/ml), and mix.

12.2.10 Silver Nitrate Solution — Dissolve 5 g silver nitrate in water and dilute to 1 000 ml.

12.2.11 Potassium Permanganate Solution — Dissolve 2.5 g of potassium permanganate in water and dilute to 100 ml.

12.2.12 Potassium Nitrite Solution — Dissolve 1 g of potassium nitrite in water and dilute to 100 ml.

12.2.13 Potassium Dichromate — Solid.

12.2.14 Ammonium Iron (II) Sulphate — Approximately 0.17 N standard volumetric solution.

12.2.14.1 Preparation

Dissolve 65 g of ammonium iron (II) sulphate in 500 ml water in a 1 000 ml volumetric flask. When dissolution is complete add 100 ml of sulphuric acid solution (*see 12.2.8*), cool, make up to the mark and mix.

12.2.14.2 Standardization

Transfer 1.000 ± 0.002 g of potassium dichromate (*see 12.2.13*) to a 500 ml beaker. Dissolve in 100 ml water, add 30 ml of sulphuric acid solution (*see 12.2.8*) and dilute to 300 ml. Proceed as described in **12.4.2.3** and **12.4.2.4**.

The chromium equivalent, T , of the ammonium iron (II) sulphate solution, expressed, in g, of chromium corresponding to 1 ml of solution is given by the formula

$$T = \frac{0.35335}{V_1}$$

where

T = chromium equivalent; and

V_1 = volume of the ammonium iron (II) sulphate solution added, in ml.

12.3 Apparatus

Usual laboratory equipments and in particular the following:

- Crucible of capacity 40 ml of iron, nickel, zirconium alumina or porcelain.
- Beaker of capacity 500 ml.
- Potentiometer* — Any high-impedance volt meter of the type used for pH measurements is suitable.
- Calomel/Platinum electrodes.
- Magnetic stirrer.

12.4 Procedure

12.4.1 Test Portion

Weigh accurately 0.5 g sample.

12.4.2 Determination

12.4.2.1 Dissolution of high carbon ferrochrome.

Place the test portion of the sample (*see 12.4.1*) in the

crucible (*see* 12.3.1) containing 8 g of sodium peroxide (*see* 12.2.1) and 4 g of sodium carbonate (*see* 12.2.2), and mix carefully. Holding the crucible in tongs, swirl it over it a flame, heating gently at first, then more strongly until fusion is complete and particles of metal disappear from the bottom of the crucible (approximately 6 min). Allow the crucible to cool.

Place the crucible in the beaker (*see* 12.3.2). Add carefully approximately 150 ml water and cover it with a watch glass. Heat carefully and, after effervescence has ceased, allow to cool. Add 40 ml sulphuric acid solution (*see* 12.2.8). When the solution is completely clear, rinse the watch glass with a jet from a wash bottle and remove the crucible after having thoroughly washed it with water. Dilute the solution to approximately 300 ml.

12.4.2.1.1 Dissolution of low carbon ferrochromium (0.5 percent carbon maximum) soluble in acids

Transfer the test portion of the sample (*see* 12.4.1) to the beaker (*see* 12.3.2). Add 25 ml sulphuric acid solution (*see* 12.2.8) and heat very gently, avoiding reduction in volume, for 20 min or until solvent action has apparently ceased.

NOTE — It is important to ensure that the whole of the test portion sample is covered by the acid and that no particles adhered to the wall of the beaker during transfer of the test portion or following shaking of the beaker during dissolution). Add 500 ml phosphoric acid (*see* 12.2.5) and evaporate just to fuming. Cool, add 40 ml cold water, heat to boiling, oxidized with nitric acid (*see* 12.2.6) and boil for 2 min. Dilute to 400 ml with hot water.

12.4.2.1.2 Dissolution ferro-silico-chromium — 1 percent C Max, soluble in acids.

Place the test portion of the sample (*see* 12.4.1) in a platinum dish, add 10-15 ml of the hydrofluoric acid (*see* 12.2.7) and, carefully drop by drop, 15 ml of the nitric acid (*see* 12.2.6). Heat the contents of the dish until the test portion is completely decomposed. Add 20 ml of sulphuric acid solution (*see* 12.2.8), and 5 ml of phosphoric acid solution (*see* 12.2.5) and evaporate until sulphuric acid fumes appear. Cool the dish, rinse the walls with water and again evaporate until sulphuric acid fume appear. Cool the dish, dissolve the salt in 40-60 ml water and transfer the solution into a 500 ml beaker. Rinse the dish with water and collect the washings in the beaker. Dilute to 300 ml and heat until dissolution of salts is complete.

12.4.2.2 Add 20 ml of the silver nitrate solution (*see* 12.2.10), 3 drops of potassium permanganate solution (*see* 12.2.11), and 8 g of ammonium persulphate (*see* 12.2.3) and boil for 10 min.

NOTE — If the colour of the permanganate acid doesn't develop after boiling for 5 min, make 0.5 g additions of ammonium persulphate to the hot solution until the colour is obtained).

Add 0.5 ml of the hydrochloric acid solution (*see* 12.2.9) to reduce excess permanganate and continue to boil for 5 min after the permanganate colour has disappeared. If the colour of permanganate is not discharged, repeat the above process until the colour disappears. Allow the solution to cool to room temperature.

12.4.2.3 Add 10 ml of the phosphoric acid (*see* 12.2.5) in case of dissolution as in 12.4.2.1, and 5 ml of phosphoric acid in case of dissolution as in 12.4.2.1.1 and 12.4.2.1.2. Set up the stirrer (*see* 12.3.5). Place the electrodes (*see* 12.3.4) in the solution and connect them to the potentiometer (*see* 12.3.3).

12.4.2.4 Titrate with ammonium iron (II) sulphate solution (*see* 12.2.14), with continuous stirring, to potential deflection of about 200 mV. The amount of iron (II) sulphate solution used corresponds to chromium and vanadium (V_2).

NOTE — If the chromium content of the sample exceeds 31 percent (m/m), start by adding 50 ml of the ammonium iron (II) sulphate solution from a pipette; if it exceeds 68 percent (m/m), start by adding 10 ml of the ammonium iron (II) sulphate solution from a pipette.

12.4.2.5 Add the potassium permanganate solution (*see* 12.2.11) drop by drop until a distinct pink colour which lasts for more than 1 min is obtained.

NOTE — The appearance of the pink colorization indicates the re oxidation of vanadium. This may also be recognized by the corresponding increasing in potential). Add potassium nitrite solution (*see* 12.2.12) drop by drop until the permanganate colour disappears and a change in potential is observed, then 2 drops in excess. Add approx. 0.5 g of urea (*see* 12.2.4) to destroy excess nitrite. Titrate with ammonium iron (II) sulphate solution to a potential deflection. This titration correspond to the vanadium content (V_3).

12.5 Expression of Results

The chromium content, expressed as a percentage by mass, is given by the formula

$$\text{Chromium content} = \frac{100T(V_2 - V_3)}{m}$$

where

T = chromium equivalent of the ammonium iron (II) sulphate solution (*see* 12.2.14), expressed of chromium corresponding to 1 ml of solution, in g;

V_2 = volume of the ammonium iron (II) sulphate solution (*see* 12.2.14) used in the first titration (chromium + vanadium), in ml;

V_3 = volume of the ammonium iron (II) sulphate solution (*see* 12.2.14) used in the second titration (vanadium), in ml; and

M = mass of the test portion, in g (*see* 12.4.2.1).

12.6 Test Report

The test report shall include the following particulars:

- a) Reference of the method used; and
- b) Results and the method of expression used.

13 DETERMINATION OF PHOSPHORUS IN THE RANGE OF 0.01 TO 0.06 PERCENT IN FERROCHROMIUM/CHARGE CHROMIUM BY ALKALIMETRIC METHOD

13.1 Outline of the Method

Sample is digested with hydrochloric acid (HCl) and nitric acid (HNO₃) acid and fumed with perchloric acid. During fuming phosphorus (P) and chromium (Cr) are oxidized. Subsequently oxidized chromium is removed as chromylchloride on addition of hydrochloric acid. Phosphorus present as orthophosphate is precipitated as ammonium phosphomolybdate and determined by alkalimetric titration.

13.2 Reagents

13.2.1 Concentrated Nitric Acid — rd = 1.42 (see IS 264).

13.2.2 Hydrofluoric Acid 48 percent — rd = 1.16.

13.2.3 Perchloric Acid — 60 percent.

13.2.4 Concentrated Hydrochloric Acid — Sp. Gr. 1.16 (see IS 265).

13.2.5 Ammonium Nitrate Solution — 50 percent (w/v).

13.2.6 Ammonium Molybdate Solution

- a) Weight 50 g of ammonium molybdate in a 500 ml beaker, add 100 ml of ammonium hydroxide, dissolve and make up to 200 ml. Keep it separately.
- b) Add 400 ml of nitric acid to 400 ml of distilled water in a 1 litre conical flask, cool and keep it separately.

Slowly add solution, a) into solution, b) with continuous stirring and cooling. Allow to settle and filter before use.

13.2.7 Potassium Nitrate Wash Solution — 2 percent (w/v).

13.2.8 Standard Nitric Acid — 0.075 N. Take 4.7 ml of concentrated nitric acid (rd = 1.42) to a 1 litre volumetric flask and make to the mark. Standardize the solution against standard sodium carbonate solution using methyl orange as indicator.

13.2.9 Standard Sodium Carbonate Solution — 0.075 N. Weigh 0.3975 g preheat sodium carbonate from 250 to 270 °C for 30 min. Cool in a desiccator, and transfer into a 100 ml volumetric flask. Dissolve in distilled water and make up to the mark.

13.2.10 Methylorange — Dissolve 0.05 g in 100 ml distilled water.

13.2.11 Phenolphthalein — Dissolve 0.5 g in 50 ml alcohol and dilute with 50 ml distilled water with constant stirring.

13.2.12 Hydrochloric Acid — 1: 3 (v/v).

13.2.13 Sodium Hydroxide Solution — Approximately 0.075 N. Dissolve 3 g of sodium hydroxide in 1 litre of distilled water.

13.3 Procedure

13.3.1 Weigh 2 g dried and agated sample (for P 0.01 to 0.03 percent) or 1 g (for P 0.03 percent above) agated sample and transfer to 500 ml teflon beaker. Add 5 ml hydrofluoric acid followed by 10 ml nitric acid. Heat the contents on a hot plate. After about 30 min, add 10 ml of perchloric acid and reflux for 30 min, after fuming starts. Again add 30 ml of perchloric acid and continue fuming on a hot plate till the mass almost dissolves. Cool the beaker and dissolve the salts with minimum quantity of water and transfer the contents into a conical flask of 500 ml capacity. Clean the bottom of the flask with a little concentrated hydrochloric acid and boil. If there is still any residue left undissolved, add 2 drops of hydrofluoric acid and 10 ml of perchloric acid and continue fuming till dense white fumes come out.

NOTE — Below –200 Mess preferably in case of high carbon ferrochrome.

13.3.2 Add concentrated hydrochloric acid (see 13.2.4) drop wise till brown fumes come out. Keep on hot plate and again reflux for some time to reoxidize chromium. Again add hydrochloric acid to remove chromium.

13.3.3 Continue the operation (see 13.3.2) till all chromium is expelled, that is, no more brown fumes on addition of hydrochloric acid.

13.3.4 Evaporate the bulk to syrupy condition. Dissolve the salts with about 50 ml of water. Add 25 ml of ammonium nitrate solution and 50 ml ammonium molybdate solution. Warm the content to 65°C with constant shaking. Remove from the heat and shake further for about 5 min. Phosphorus is precipitated as fine yellow crystal. Allow the precipitate to settle for 2 h at least.

13.3.5 Filter the precipitate on a paper pulp pad, wash the flask and precipitate several times with cold neutral potassium nitrate wash solution until the washings tested no longer acidic to phenolphthalein (see Note). Transfer the precipitate with pad to the original flask where phosphorus was precipitated. Add 10 to 15 ml of distilled water and shake the flask to dislodge the pad. Add 10 ml of sodium hydroxide solution to the flask and shake well. Titrate the excess sodium hydroxide solution with standard acid using phenolphthalein as indicator.

NOTE — 10 ml of final washing collected in a test tube should give pink colour with phenolphthalein by a drop of sodium hydroxide solution of approximately 0.075 N. Normally the precipitate is washable free from acid by giving about 5 to 6 washings.

13.3.6 Carry out a reagent blank with same quantity of all the reagents chemicals used except the sample.

13.4 Calculation

$$\text{Phosphorus, percent} = \frac{(V_1 - V_2) \times N \times 0.00135 \times 100}{M}$$

where

V_1 = volume of standard nitric acid required by the blank, in ml;

V_2 = volume of standard nitric acid required in the test sample, in ml;

N = normality factor of standard nitric acid used; and

M = mass of the sample taken, in g.

14 DETERMINATION OF PHOSPHORUS BY SPECTROPHOTOMETRIC METHOD IN MEDIUM/HIGH CARBON FERRO-CHROMIUM AND CHARGE CHROME (CONTAINING CARBON ABOVE ONE PERCENT AND PHOSPHORUS UP TO 0.05 PERCENT MAX)

14.1 Outline of the Method

Sample is fused with sodium peroxide and leached in 100 ml of distilled water and neutralized with concentrated hydrochloric acid. Separate chromium by precipitation of R_2O_3 group. Treat the precipitate with nitric and perchloric acids along with filter paper. Fumigate while expelling chromium as chromyl chloride fumes by adding sodium chloride salt. Separate silica by filtration. The phosphorus in the solution is reacted with ammonium molybdate and reduced with hydrazine sulphate solution to give molybdenum blue. The intensity of colour is measured spectrophotometrically at 820 nm.

14.2 Reagents

14.2.1 Sodium Peroxide — Granules.

14.2.2 Sodium Carbonate — Anhydrous solid.

14.2.3 Hydrochloric Acid — rd = 1.16 (see IS 265).

14.2.4 Nitric Acid — rd = 1.42 (see IS 264).

14.2.5 Perchloric Acid — 60 percent.

14.2.6 Aqua Ammonia

14.2.7 Sodium Chloride — Solid.

14.2.8 Sodium Meta Bisulphite — 10 percent (m/v) solution should be freshly prepared.

14.2.9 Ammonium Molybdate Solution — Solution A — Add 20 g of ammonium molybdate $[(NH_4)_6 MO_7 O_{24} H_2 O]$ to 100 ml of warm water. Add 800 ml of dilute sulphuric acid (3:5) (previously prepared and cooled) and cool to room temperature. Make up the volume to 1 litre with distilled water.

14.2.10 Hydrazine Sulphate Solution — Solution B. Dissolve 1.5 g of hydrazine sulphate ($N_2 H_4 H_2 SO_4$) in water and dilute to 1 litre.

14.2.11 Phosphorus Standard Solution (1 ml = 5mg P) — Weigh accurately 2.292 g of anhydrous $Na_2 HPO_4$ (previously dried at 105 °C) and transfer to 1 000 ml volumetric flask. Dissolve in 100 ml of water, dilute and make up to the mark and mix. Pipette out 10 ml of solution and dilute to 1 000 ml with water.

14.2.12 Colour Development Solution — Mix 25 ml of solution A and 10 ml of solution B and make up the volume to 100 ml with water. This should be prepared just before use.

14.3 Procedure

14.3.1 Weigh accurately 0.5 g of sample into 50 ml nickel crucible add 8 g of sodium peroxide and 1 g sodium carbonate and mix well. Heat carefully over a low temperature and finally fuse the mass over a flame till completely fused.

14.3.2 Cool the crucible to room temperature and transfer the same to 400 ml beaker containing 100 ml of hot water. Dissolve the cake and clear the crucible and wash it well into the same beaker. Add about 40 ml of hydrochloric acid to neutralize the solution (till the precipitate dissolves). Add 5 ml nitric acid and boil the solution for 1 min. Neutralize the solution with aqua ammonia and add excess about 10 ml, cool under 60 °C. Filter using whatman No. 4 filter paper. Wash $R_2 O_3$ with hot water 5 or 6 times till we find the filtrate colourless.

14.3.3 Transfer the paper with precipitate into the original beaker. Add 20 ml of nitric acid and 15 ml of perchloric acid and heat to dissolve the precipitate and filter paper. Evaporate to fumes of perchloric acid and oxidise the chromium remained. Add 1 g of sodium chloride to expel the chromium and repeat expulsion to avoid chromium. Heat to white fume to vaporise the chromium.

14.3.4 Cool, add 40 ml of water and boil to dissolve the soluble salts. Cool the solution Transfer to 100 ml volumetric flask and make up to the mark. Filter through Whatman No.1 filter paper to eliminate silicon. Discard filtrate of initial stage and then collect into a dried beaker.

14.3.5 Take an aliquot of 10 ml of filtrate, that is 0.05 g

into a 250 ml beaker in duplicate. Add 10 ml of 5 percent sodium metabisulphite solution (freshly prepared) and 10 ml of water and boil for 1 min.

14.3.6 Add 25 ml of colour development solution and immerse the beaker in a boiling water bath and keep it for 10 min for full colour development. Cool to room temperature, transfer to 100 ml volumetric flask and make up to the mark with distilled water and shake well.

14.3.7 Transfer a suitable portion of **14.3.6** to measuring cell and adjust the spectro photometer wavelength at 820 nm and measure the absorbance the reagent blank.

14.3.8 Blank

Carry out a blank determination using same amount of reagents and chemicals and following the procedure specified in **14.3.1** to **14.3.7**.

14.3.9 Preparation of Calibration Curve

Transfer 0, 1, 2, 3, 4 and 5 ml of standard phosphorus solution (1 ml = 5 mg P) (see **14.2.11**) to 250 ml beaker and proceed according to **14.3.6** and **14.3.7**. The flask containing zero ml of phosphorus solution is regarded as blank and the net value of spectrophotometric reading is plotted against mg of phosphorus.

14.3.10 Convert the spectrophotometric readings of test solution to mg of phosphorus obtained from calibration curve and calculate the percentage of phosphorus.

14.3.11 Also carry out certified standard sample in the same range to verify the accuracy in the same procedure.

14.4 Calculation

$$\text{Phosphorus, percent by mass} = \frac{A - B}{W} \times \frac{100}{10^6}$$

where

A = mass of phosphorus found in solution, in mg;

B = mass of phosphorus found in reagents, in mg; and

W = mass of the sample taken, in g.

15 DETERMINATION OF MANGANESE BY SPECTROPHOTOMETRIC METHOD IN MEDIUM/HIGH CARBON FERRO-CHROMIUM AND CHARGE CHROME (CONTAINING CARBON ABOVE ONE PERCENT, AND MANGANESE UP TO ONE PERCENT)

15.1 Outline of the Method

Sample is fused with sodium peroxide and leached in 100 ml of distilled water, neutralise with 30 percent

sulphuric acid and precipitate R_2O_3 group adding ammonium chloride and ammonium hydroxide and then add ammonium persulphate to the R_2O_3 group to precipitate manganese as MnO_2 . Treat the precipitate with nitric and perchloric acids along with filter paper. Fumigate while expelling residual chromium as chromile chloride fumes by adding sodium chloride salt. Separate silica by filtration. Take an aliquot of 0.1 g and develop manganese colour (pink colour) by ammonium persulphate oxidation. The intensity of colour is measured spectrophotometrically at 525 nm.

15.2 Reagents

15.2.1 Sodium Peroxide — Granules.

15.2.2 Sodium Carbonate — Anhydrous solid.

15.2.3 Dilute Sulphuric Acid — 30 percent (v/v).

15.2.4 Ammonium Persulphate — Solid.

15.2.5 Silver Nitrate Solution — 1 percent (w/v).

15.2.6 Phosphoric Acid — rd = 1.75 or 88 percent (Manganese free).

15.2.7 Potassium Permanganate Solid

15.2.8 Nitric acid — rd = 1.42 (see IS 262).

15.2.9 Perchloric Acid — 60 percent.

15.2.10 Aqua Ammonia

15.2.11 Ammonium Chloride — Solid.

15.2.12 Sodium Chloride — Solid.

15.2.13 Manganese Standard Solution (1 ml = 100 mg of Mn) — Weigh accurately 0.7186 g of potassium permanganate in 500 ml volumetric flask. Dissolve in distilled water and make up to the mark. Pipette out 20 ml solution to 100 ml volumetric flask and make up to the mark with distilled water (1 ml = 100 mg of Mn).

15.3 Procedure

15.3.1 Weigh accurately 0.5 g of sample into 50 ml nickel crucible add 8 g of sodium peroxide and 1 g of sodium carbonate and mix well. Heat carefully over a low temperature and finally fuse the mass over a flame till completely fused.

15.3.2 Cool the crucible to room temperature and transfer the same to 400 ml beaker containing 100 ml distilled water to dissolve the mass from the crucible and wash the crucible boil and cool.

15.3.3 Add 30 percent sulphuric acid (H_2SO_4) just to neutralize and boil to get clear solution. Precipitate R_2O_3 adding ammonium chloride and ammonium Hydroxide and then add ammonium persulphate (30 ml of 20 percent), 30 ml ammonium hydroxide boil and

filter through Whatman No. 4 filter paper. Wash R_2O_3 with hot water 5 or 6 times to get colourless filtrate.

15.3.4 Transfer the paper with precipitate into the original beaker. Add 20 ml of nitric acid and 15 ml of perchloric acid and heat to dissolve the precipitate and filter paper. Evaporate to fumes of perchloric acid and oxidise the chromium, if any and add a pinch of sodium chloride salt to expel the chromium, if any as chromyl chloride fumes.

15.3.5 Cool and add 40 ml of water and boil to dissolve the soluble salts. Cool the solution and transfer to 100 ml volumetric flask and make up to the mark. Filter through Whatman No.1 filter paper to eliminate silicon. Discard the rinse solution and then collect filtrate into a dried beaker.

15.3.6 Take an aliquot of 0.1 g (20 ml of solution) into a 250 ml beaker in duplicate. Oxidise to permanganic acid by adding sulphuric acid (10 ml of 10 percent) orthophosphoric acid (10 ml of 10 percent), ammonium persulphate (10 ml of 20 percent) and silver nitrate (5 ml of 1 percent). Boil for 2 min, cool and transfer to 100 ml volumetric flask and make up to the mark.

15.3.7 Transfer a suitable portion of **15.3.5** to measuring cell and adjust spectrophotometer wavelength at 525 nm and measure the absorbance against the reagent blank.

15.3.8 Blank

Carry out a blank determination using same amount of reagents and chemicals and following the procedure specified in **15.3.1** to **15.3.6**.

15.3.9 Also carry out certified standard sample to verify the accuracy, in the same procedure.

15.3.10 Preparation of Calibration Curve

Transfer 0, 1, 2, 3, 4, 5 and 6 ml of standard manganese solution (see **15.2.13**) into 250 ml beakers and add 10 ml of 10 percent H_2SO_4 and 1 ml of 5 percent sodium-oxalate solution. Boil for 2 min and add orthophosphoric acid (10 ml of 10 percent) and silver nitrate (5 ml of 1 percent) and ammonium persulphate (10 ml of 20 percent). Boil for about 2 min; cool and make up to 100 ml volumetric flask and proceed as per **15.3.6**.

15.3.11 Convert the spectrophotometric readings of test solution to mg of Mn obtained from calibration curve and calculate the percentage of Mn.

15.4 Calculation

$$\text{Manganese, percent by mass} = \frac{A - B}{W} \times \frac{100}{10^6}$$

where

A = manganese found in final test solution, in mg;

B = manganese found in final reagent solution, in mg; and

W = weight of the sample taken, in g.

16 DETERMINATION OF TITANIUM BY SPECTROPHOTOMETRIC METHOD IN MEDIUM/HIGH CARBON FERROCHROMIUM AND CHARGE CHROME (CONTAINING CARBON ABOVE 1 PERCENT AND TITANIUM UPTO 0.5 PERCENT)

16.1 Outline of the Method

Sample is fused with sodium peroxide and leached in 100 ml of distilled water and neutralised with concentrated hydrochloric acid. Separate chromium by precipitation of R_2O_3 . Treat the precipitate with nitric and perchloric acids along with filter paper. Fumigate while expelling residual chromium as chromyl chloride fumes by adding sodium chloride salt. Separate silica by filtration. The titanium in the solution is reacted with sulphuric acid (H_2SO_4), phosphoric acid (H_3PO_4) and hydrogen peroxide (H_2O_2) solutions to develop yellow colour. The intensity of colour is measured spectrophotometrically at 418 nm.

16.2 Reagents

16.2.1 Sodium Peroxide — Granules.

16.2.2 Sodium Carbonate

16.2.3 Hydrochloric Acid — rd = 1.16 (see IS 265).

16.2.4 Dilute Hydrochloric Acid — 1:1 (v/v).

16.2.5 Nitric Acid — rd = 1.42 (see IS 264).

16.2.6 Perchloric Acid — 60 percent.

16.2.7 Aqua Ammonia

16.2.8 Sodium Chloride — Solid.

16.2.9 Sulphuric Acid

16.2.10 Orthophosphoric Acid

16.2.11 Hydrogen Peroxide Solution — 30 percent.

16.2.12 Titanium Standard Solution (1 ml = 100 mg of Ti) — Weigh accurately 0.834 0 g of titanium oxide into 250 ml beaker. Dissolve in concentrated H_2SO_4 , cool and dilute to make up to 1 000 ml volumetric flask. Pipette out 20 ml solution to 100 ml volumetric flask make up to the mark with distilled water (1 ml = 100 mg Ti).

16.2.13 Sodium Hydroxide — 10 percent (w/v) solution.

16.2.14 Ammonium Nitrate — Wash solution 2 percent (w/v).

16.3 Procedure

16.3.1 Weigh accurately 0.5 g of sample into 50 ml nickel crucible add 8 g of sodium peroxide and 1 g sodium carbonate and mix well. Heat carefully over a low temperature and finally fuse the mass over a flame till completely fused.

16.3.2 Cool the crucible to room temperature and transfer the same to 400 ml beaker containing 100 ml of hot water. Dissolve the cake and clear the crucible and wash it well into the same beaker. Add about 40 ml of hydrochloric acid to neutralize the solution (till the precipitate dissolves).

16.3.3 Add 5 ml nitric acid and boil the solution for 1 min. Neutralize the solution with aqua ammonia and add excess about 10 ml, to precipitate R_2O_3 , cool under 60 °C. Filter through whatman No. 4 filter paper. Wash R_2O_3 with hot water 5 or 6 times till we find the filtrate colourless.

16.3.4 Dissolve the precipitate in minimum quantity of 1:1 dilute HCl, wash the funnel with hot 1:1 hydrochloric acid (HCl). To the solution add sodium hydroxide 10 percent solution till precipitation followed by 3 ml of 30 percent hydrogen peroxide (v/v) and boil the contents for 5 minutes. Filter and wash the precipitate with 2 percent ammonium nitrate solution.

NOTE — This procedure is required to separate vanadium from titanium.

16.3.5 Cool, add 40 ml of water and boil to dissolve the soluble salts. Cool the solution, transfer to 100 ml volumetric flask and make up to the mark. Filter through Whatman No.1 filter paper to eliminate silicon and discard filtrate of initial stage and then collect into a dried beaker.

16.3.6 Take an aliquot of 50 ml that is 0.25 g into 100 ml volumetric flasks and add 10 ml of 10 percent sulphuric acid and 10 ml of 10 percent orthophosphoric acid, mix well and add 10 ml of 10 percent hydrogen peroxide solution and dilute to make up to the mark and shake well to get yellow pertitanic acid.

16.3.7 Transfer a suitable portion of **16.3.5** to measuring cell and adjust the spec-trophoto meter wavelength at 418 nm and measure the absorbance against the reagent blank.

16.3.8 Blank

Carry out a blank determination using same amount of reagents and chemicals and following the procedure specified in **16.3.1** to **16.3.7**.

16.3.9 Also carry out certified standard sample to verify the accuracy, in the same procedure.

16.3.10 Preparation of Calibration Curve

Transfer 0, 2, 4, 6, 8 and 10 ml of standard titanium

solution into 100 ml volumetric flasks and add 10 ml of 10 percent sulphuric acid, 10 ml of 10 percent orthophosphoric acid and 10 ml of 10 percent hydrogen peroxide solutions, dilute to make up to the mark and shake well. Read out the absorbance readings for corresponding concentrations of Ti on spectrophotometer at 418 nm. Draw a graph of absorbance against concentration.

16.3.11 Convert the spectrophotometric readings of test solution to mg of Titanium obtained from calibration curve and calculate the percentage of titanium.

16.4 Calculation

$$\text{Titanium, percent by mass} = \frac{A - B}{W} \times \frac{100}{10^6}$$

where

A = Ti found in final test solution, in mg;

B = Ti found in the reagent solution, in mg; and

W = weight of the sample taken, in g.

17 DETERMINATION OF CHROMIUM CONTENT IN FERROCHROME BY X-RAY FLUORESCENCE SPECTROPHOTOMETRIC METHOD IN THE RANGE OF PERCENT

17.1 Outline of the Method

The ferrochromium (Fe-Cr) powder samples are made to a press pellet with a binder in a pelletising machine. The plane surface of the pellet so obtained is exposed to primary X-ray. The secondary fluorescence radiation from the sample pellet is dispersed by means of crystal and the intensity measured by detector at selected wavelength. Regression graph is made taking standard reference materials of known composition and the concentration of chromium in the unknown sample is determined by correlating with the above standard graph.

17.2 Equipments and Accessories

Pulverizer, electronic balance, pelletizer, aluminum cup, cellulose or methyl cellulose as binder, boric acid as bottom filler, press cork made of rubber and a wave length dispersive XRF spectrometer.

17.3 Pulverizer

It consists of a grinding vessel (100 cc) made of Cr-Si or W-C, that can be set in to vibration of high frequency so that the pieces of samples place in it can be powdered in to 200 mesh size in 3-4 min.

17.4 Electronic Balance

A single pan electronic balance having readability up to 4th place of decimal with ± 0.01 mg. accuracy is required.

17.5 Pelletizer

A pelletizer equipped with a gauge enabling reproducible pressure up to 40 tonne.

17.5.1 *Al-cup, Cellulose or Methyl Cellulose, Boric Acid and Pressing Cork*

Al-cup should be made of pure aluminium (Al). Cellulose or methyl cellulose and boric acid should be of Analytical Reagent (AR) or Guaranteed Reagent (GR) quality.

Pressing cork should be made of rubber or any non-corrosive soft material having diameter of 45 mm.

17.6 WD-XRF Spectrometer

17.6.1 X-ray spectrometer, designed for X-ray emission analysis using vacuum medium, sample chamber. The optics should consists of beam filter, mask, collimator, crystal, goniometer and detector (parallel geometry) or fixed channels (monochromators) consists of slits and detectors (focusing geometry). X-ray tube should be of Rh target which acts as source of primary x-rays. The spectrometer chamber houses all the optics and should be under vacuum. Beam filter, is used to reduce any unwanted and background radiations, also to improve signal to noise ratio. Collimator is used for limiting the characteristic X-rays to parallel when using flat crystal. For curved crystal instead of collimator, slits are used.

17.6.2 Analyzing crystals, flat or curved lithium fluoride (LiF200/LiF220) is used as a dispersion medium to separate the characteristic wavelength analyzed. Detector may be Flow Proportional Counter (FPC) or a sealed detector which measures and quantifies the analyzed intensities. The counting electronics should have dual multi-channel analyzer for faster counting and digital signal processor for dynamic corrections of dead time losses and pulse shrinkage.

The sample chamber should be under vacuum environment. It should have an intermediate small chamber for medium changeover during sample introduction. Sample can be introduced into the sample chamber by means of a mechanical arm.

17.6.3 The computer and associated electronic circuits interact with different parts of the spectrometer to control various sequences of operations and also to carry out the mathematical computation to display/print out the final results in terms of percentage.

17.7 Standards

17.7.1 Primary standards, certified reference materials of ferrochromium (Fe-Cr) of known compositions as near in composition to the sample to be analyzed shall be used as standards for preparing the calibration curve. The standards selected for the calibration must be

within ± 10 percent of the Cr content of the unknown sample to be analyzed.

17.7.2 Secondary standards are not available from commercial sources. Generate secondary standards in the laboratory by wet chemical method to cover the entire analytical concentration ranges. Select a minimum of five samples that covers the entire range and analyze these samples wet chemically preferably by more than one chemist and use the average chemical value for the calibration.

17.8 Preparation of XRF Spectrometer

Follow the XRF manufacturer's instruction for the conditioning and preparation of XRF unit.

17.9 Setting Up the XRF Instrument

Two numbers of ferrochromium (Fe-Cr) standards/setting up samples (SUS), one containing high and other containing low percent chromium (Cr) content should be used for setting up the instrument.

17.10 Drift Correction

The intensities from the above setting up standards as described in **17.17**, are stored in the computer operating software along with the calibration curve. Before analyzing the unknown samples, it is necessary to update the intensities, to take care any drift in the spectrometer.

17.11 Reagents

Only high purity anhydrous chemicals such as boric acid, cellulose or methyl cellulose should be used for the pellet sample preparation. Detector gas, usual gas composition for P-10 gas used in FPC detector is 90 percent argon and 10 percent methane. Binders, used for pressed pellet should not contribute any spectral interference.

17.12 Sample Preparation

Samples are prepared by pelletizing with binder. One of the methods is as follows:

Weigh 10.0 g of the powdered ferrochromium (Fe-Cr) sample of 200 mesh size and 1.0 g of cellulose or methyl cellulose and transfer quantitatively to a clean mill container for grinding and mixing. The mill container is kept inside the pulverizer machine and pulverized for 1 min. The mixture is then taken out in to a clean polyethylene paper and evenly spread over an Al-cup, containing 2/3 filled with boric acid. The upper surface is pressed with a rubber cork and the outer surface of the filled Al-cup cleaned with cotton holding the Al-cup and the cork in the upright position. Then it is pressed in the pelletizing machine for 1 min at 30 tonne pressure. The sample pellet is taken out and it is ready for excitation in a XRF spectrometer.

All calibration standards and the unknowns to be used with them must be prepared in exactly the same manner.

Whichever method of preparation is used, it is essential that a smooth, uniform, and flat surface is exposed to X-ray radiation.

17.13 Calibration of XRF Spectrometer

The calibration of the XRF spectrometer will be done by taking different certified reference ferrochromium (Fe-Cr) standards (Primary or secondary standards) of known composition. The press pellets are prepared as per the procedure described in 17.5.

Select the crystal, x-ray line and detector as shown in the Table 1.

The collimators, filter and excitation potential (kV, mA), etc, are suitably selected to obtain the optimum sensitivity of the selected line.

The calibration standards are to be irradiated 2 times each and their average intensity values are to be taken for calibration. The regression curve is to be established

Table 1 Selection of Spectrometer Parameters
(Clause 17.13)

Element Channel (1)	X-ray Line (2)	Crystal (3)	Detector (4)
Cr	Ka	LiF 200	FPC/Sealed

by taking the intensities and corresponding concentration values of various standards used.

The concentration of the unknown sample can be measured by referring to this regression curve which is stored in the computer.

17.14 Precision and Accuracy

Precision of this test method to be determined by running one sample subsequently 20 times to obtain the relative standard deviation. Precision can be improved by using system with higher sensitivity or by increasing the analysis time.

Determine the accuracy by running one of the CRM standards or secondary standards as unknown.

Bureau of Indian Standards

BIS is a statutory institution established under the *Bureau of Indian Standards Act*, 2016 to promote harmonious development of the activities of standardization, marking and quality certification of goods and attending to connected matters in the country.

Copyright

BIS has the copyright of all its publications. No part of these publications may be reproduced in any form without the prior permission in writing of BIS. This does not preclude the free use, in the course of implementing the standard, of necessary details, such as symbols and sizes, type or grade designations. Enquiries relating to copyright be addressed to the Director (Publications), BIS.

Review of Indian Standards

Amendments are issued to standards as the need arises on the basis of comments. Standards are also reviewed periodically; a standard along with amendments is reaffirmed when such review indicates that no changes are needed; if the review indicates that changes are needed, it is taken up for revision. Users of Indian Standards should ascertain that they are in possession of the latest amendments or edition by referring to the latest issue of 'BIS Catalogue' and 'Standards : Monthly Additions'.

This Indian Standard has been developed from Doc No.: MTD 34 (5219).

Amendments Issued Since Publication

Amend No.	Date of Issue	Text Affected

BUREAU OF INDIAN STANDARDS

Headquarters:

Manak Bhavan, 9 Bahadur Shah Zafar Marg, New Delhi 110002

Telephones : 2323 0131, 2323 3375, 2323 9402

Website: www.bis.org.in

Regional Offices:

Telephones

Central	: Manak Bhavan, 9 Bahadur Shah Zafar Marg NEW DELHI 110002	{ 2323 7617 2323 3841
Eastern	: 1/14 C.I.T. Scheme VII M, V. I. P. Road, Kankurgachi KOLKATA 700054	{ 2337 8499, 2337 8561 2337 8626, 2337 9120
Northern	: Plot No. 4-A, Sector 27-B, Madhya Marg, CHANDIGARH 160019	{ 26 50206 265 0290
Southern	: C.I.T. Campus, IV Cross Road, CHENNAI 600113	{ 2254 1216, 2254 1442 2254 2519, 2254 2315
Western	: Manakalaya, E9 MIDC, Marol, Andheri (East) MUMBAI 400093	{ 2832 9295, 2832 7858 2832 7891, 2832 7892

Branches: AHMEDABAD. BENGALURU. BHOPAL. BHUBANESWAR. COIMBATORE. DEHRADUN. DURGAPUR. FARIDABAD. GHAZIABAD. GUWAHATI. HYDERABAD. JAIPUR. JAMMU. JAMSHEDPUR. KOCHI. LUCKNOW. NAGPUR. PARWANOO. PATNA. PUNE. RAIPUR. RAJKOT. VISAKHAPATNAM.

Published by BIS, New Delhi